EXHIBIT 8

Table III. Mass Spectra[a] of Cyclic Silanes

Ion	$(CH_2)_4SiH_2$[b]	$(CH_2)_3SiH_2$[d]
M + 1	...	1.3
M	9.4	12.3
M − 1	3.0	7.1
M − 2	1.5	8.1
M − CH_2 + 1	...	2.1
M − CH_3	0.9	4.3
M − CH_2 − 2	...	1.4[e]
M − CH_2 − 3	...	4.1[e]
M − CH_2 − 5	...	2.6[e]
M − $2CH_2$ + 1	...	7.0
M − 28	48.3	13.6
M − 29	4.8	10.8
M − 30	~3[c]	6.9
M − 31	4.4	3.3
M − 33	~2[c]	4.0[e]
SiH_3^+	...	5.1
SiH_2^+	...	0.6
SiH^+	4.5	4.3
Si^+	3.1	14.5
M − CH_2SiH_2	1.4	

[a] Spectra at 70-v ionizing voltage; intensities given as per cent of total intensity above *m/e* 40. [b] Reference 12. [c] Estimated from given spectra. [d] Corrected to spectra expected for ^{28}Si, ^{12}C, ^{1}H. [e] Peaks that have essentially vanished in spectra at 8.2-v ionization potential.

negative shift of the α protons in $(CH_2)_3SiH_2$. This effect is reduced when the silicon hydrogens are replaced by halogens; in this sense, the $SiCl_2$ group appears less electropositive than SiF_2.

Mass Spectra. Mass spectra of both $(CH_2)_3SiH_2$ and $(CH_2)_3SiD_2$ were obtained. The important ions observed at an ionizing potential of 70 v for the nondeuterated species are compared in Table III to those found for $(CH_2)_4SiH_2$ as reported by Duffield and coworkers.[12] Spectra were also obtained at lower voltages. The percentage contribution of the molecular ion to the spectrum above *m/e* of 40 increased from 12.3% at 70 v to 20.9 (15), 29.5 (10), and 36.0% (8.2 v). In the spectrum at 70 v, over one-half of all intensity is distributed between 31 and 25 *m/e*; at 8.2 v this is only about 10%.

In general, the spectrum of the four-membered ring silane is richer in the number of peaks observed than that of silacyclopentane. However, some of these additional ions in the silacyclobutane spectrum were not observed at lower ionizing potentials. Both spectra have strong molecular ion peaks; both have a large intensity at M − 28, implying a loss of ethylene. Both spectra have M − 1 and M − 2 ions resulting primarily from Si–H bond cleavage. The 1,1-d_2 analogs of each give spectra with peaks corresponding to loss of one or two deuterium atoms.

A significant difference in the spectra of the two silanes is that in silacyclobutane peaks were observed at M − $n$$CH_2$ + 1 (n = 1–3). Thus, in the four-membered ring, Si–C bond cleavage seems to be accompanied by hydrogen transfer; this process appears unimportant in silacyclopentane fragmentation.

Acknowledgments. Advice from Professors R. C. Lord and D. Seyferth is greatly appreciated. This work has been supported in part by National Science Foundation Grant GP-2111.

(12) A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 2920 (1965).

Nitrosative Cleavage of Tertiary Amines[1]

Peter A. S. Smith and Richard N. Loeppky

Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104. *Received September 6, 1966*

Abstract: Tertiary amines react with aqueous nitrous acid, contrary to common belief, and undergo dealkylation to form a carbonyl compound, a secondary nitrosamine, and nitrous oxide. The ratios of products from *meta*- or *para*-monosubstituted tribenzylamines are affected but little by the electronic influence of the substituents, and obey the Hammett equation with a small negative value of the reaction constant. Susceptibility of an amine to nitrosative cleavage is markedly reduced by base-weakening effects, and is prevented altogether by quaternization. Quinuclidine, in which the tertiary nitrogen is at a bridgehead, is inert. α substituents in tribenzylamines and benzyldiethylamines strongly shift dealkylation to the unsubstituted groups, regardless of the electronic character of the α substituent (*e.g.*, alkyl or carboethoxy). Tribenzylamine-α,α-d_2 shows a deuterium isotope effect k_H/k_D = 3.78. The facts are correlated by a mechanism (eq 4–6) involving formation of an N-nitrosoammonium ion and *cis* elimination of nitroxyl to form a ternary immonium ion, $R_2N^+{=}CR_2$, which then undergoes hydrolysis and further nitrosation. Nitrosyl fluoroborate and tribenzylamine form an unstable 1:1 addition compound at −45°; above −20°, this substance decomposes to form tribenzylammonium and N,N-dibenzylbenzaldimmonium fluoroborates.

The belief that tertiary amines do not react with aqueous nitrous acid is probably the most persistent myth in organic chemistry, notwithstanding a veritable parade of experimental refutations extending over an even century. Scarcely a textbook currently in print suggests that aught beyond salt formation occurs, and the assumed inertness of tertiary amines has been made the basis of a test for distinguishing them from primary and secondary amines.

In actual fact, Guether[2] reported correctly in 1864

(1) Presented at the XIXth I.U.P.A.C. Congress, London, 1963; from the doctoral dissertation of R. N. L.

(2) B. Guether, *Arch. Pharm.*, [2] **123**, 200 (1864).

that triethylamine is converted to diethylnitrosamine by aqueous nitrous acid. Unfortunately, he was taken to task 2 years later by Heintz[3] for allegedly having used impure amine, and Heintz went on to claim that highly purified triethylamine remained unattacked. However, Heintz used very different conditions from Guether's, and apparently paid no attention to the possibility that the occurrence of further reaction might be dependent on time, temperature, and acidity. Heintz's paper is apparently the origin of the widely accepted test mentioned above.

The history of the many independent rediscoveries of the cleavage of tertiary amines by nitrous acid has recently been reviewed by Hein,[4] and need not be repeated here. The most recent encounter with the phenomenon occurred in this laboratory, as an outgrowth of nitrosation experiments with substituted hydrazides.[5]

The accumulated reports of the cleavage of tertiary amines with nitrous acid lead to a clear generalization that an alkyl group is removed oxidatively, and appears as an aldehyde or ketone, the nitrogenous portion being converted to a nitrosamine (eq 1); further details of the stoichiometry are obscure. Three quite differ-

$$R_2N\text{-}CHR_2' \xrightarrow{HNO_2} R_2N\text{-}NO + R_2'C{=}O \qquad (1)$$

ent mechanisms have been proposed. According to one view,[6] a free-radical process may be involved, in which the amine is first oxidized to an aminium ion radical, which then fragments to secondary amine and a methylene cation radical, from which a carbonyl compound is generated by reaction with water and further oxidation by nitrosonium ion (eq 2 and 3). According

$$R_2N\text{-}CHR_2' + NO^+ \longrightarrow R_2\dot{N}^+\text{-}CHR_2' + NO \qquad (2)$$

$$R_2\dot{N}^+\text{-}CHR_2' \longrightarrow R_2NH + R_2C^+ \qquad (3)$$

$$R_2NH \xrightarrow{HNO_2} R_2N\text{-}NO \qquad R_2C^+ \xrightarrow{H_2O,\ NO^+} R_2'C{=}O + NO$$

to another view,[5] the mechanism is probably heterolytic, involving elimination of nitroxyl from a nitrosammonium ion to form an immonium ion, which is then hydrolyzed (eq 4, 5, and 6).

$$R_2N\text{-}CHR_2' \xrightarrow{HNO_2} R_2N^+(CHR_2)(NO) \longrightarrow R_2N^+{=}CR_2' + HNO \qquad (4)$$

$$R_2N^+{=}CR_2' \xrightarrow{H_2O} R_2'C{=}O + R_2N^+H_2 \xrightarrow{HNO_2} R_2N\text{-}NO \qquad (5)$$

$$2HNO \longrightarrow H_2N_2O_2 \longrightarrow H_2O + N_2O \qquad (6)$$

The third mechanism[7] involves nucleophilic dealkylation to give a secondary nitrosamine and an alcohol (or alkyl halide), analogous to the cleavage of tertiary amines with phosgene or cyanogen bromide.[8] The carbonyl compounds obtained are supposed to result from subsequent oxidation. This mechanism was originally formulated somewhat indefinitely as a four-center process, but can more reasonably be imagined as nucleophilic displacement on an α carbon of an N-nitrosoammonium ion (eq 7 and 8). It can be

$$R_2N^+(CHR_2)(NO) \xrightarrow{H_2O} R_2N\text{-}NO + R_2CHOH \qquad (7)$$

$$R_2CHOH \xrightarrow{HNO_2} R_2C{=}O + N_2O \text{ or } NO \qquad (8)$$

seen at once that the stoichiometry demanded by the respective mechanisms is different, and that the product-determining steps are of different kind. The present study of the reaction consists of investigations of the stoichiometry, structural requirements, and product selectivity, in the light of the foregoing and other reasonable mechanisms.

Results

Tribenzylamine and N,N-dibenzylaniline and their substituted derivatives were chosen for study because they are among the few simple tertiary amines that are solids at ordinary temperatures, at the same time allowing systematic variation of substituent influences. These amines were prepared in the customary way by treatment of primary or secondary amines with benzyl halides or by reductive alkylation.

It had already been shown that the cleavage of tertiary amines with nitrous acid is slow at 0° and is retarded in strongly acid medium, for which reasons warm, aqueous acetic acid was chosen as the medium in these experiments.[5] It did not seem practical to determine the stoichiometry of nitrous acid consumption directly under such conditions, owing to the instability of nitrous acid and the loss of oxides of nitrogen. One experiment was nevertheless conducted with equimolar amounts of nitrous acid (from sodium nitrite) and tribenzylamine. Unreacted amine, which could be recovered fairly efficiently, amounted to 50%, and the purified dibenzylnitrosamine obtained amounted to 38% of the original amine. The discrepancy in the material balance, 12%, is believed to be largely if not entirely a result of mechanical losses on separation and purification. Optimum yields of purified cleavage products, amounting generally to about 80% of benzaldehydes and 60% of nitrosamines, were obtained only with a large excess of nitrous acid, about 10 molar equiv.

More significant information about the stoichiometry was obtained from an experiment in which the evolved gases were collected. Nitric oxide and nitrogen dioxide, inevitably formed from the decomposition of nitrous acid, were removed by scrubbing with strongly alkaline potassium permanganate solution. There remained a volume of gas equivalent to nearly 0.5 mole per mole of amine used; mass spectrometric examination showed it to consist largely of nitrous oxide, with minor contamination by air and nitric oxide.

Some N,N-dibenzylanilines were examined in order to obtain information about the importance of the basicity of the amine. N,N-Dibenzylaniline itself could not, of course, be examined for nitrosative cleavage, since nitrosation of the aniline ring would take place rapidly; the *p*-chloro and *p*-nitro derivatives, which are free of this objection, were therefore used. N,N-dibenzyl-*p*-chloroaniline reacted smoothly under the same conditions as tribenzylamine; benzaldehyde

(3) W. Heintz, *Ann.*, **138**, 319 (1866).
(4) G. Hein, *J. Chem. Educ.*, **40**, 181 (1963).
(5) P. A. S. Smith and H. G. Pars, *J. Org. Chem.*, **24**, 1324 (1959).
(6) I. Glazer, E. D. Hughes, C. K. Ingold, A. T. James, G. T. James, and E. Roberts, *J. Chem. Soc.*, 2671 (1950).
(7) R. Wegler and W. Frank, *Ber.*, **69**, 2071 (1936); **70**, 1279 (1937).
(8) J. von Braun, *ibid.*, **33**, 1438 (1900).

(42%) and benzyl-*p*-chlorophenylnitrosamine (62%) were obtained normally, although in slightly reduced yield. Under the same conditions, N,N-dibenzyl-*p*-nitroaniline was recovered unchanged in 99% yield. N,N-Dibenzyl-*p*-anisidine and N,N-dibenzyl-*p*-toluidine were also examined; both underwent cleavage, as shown by the formation of appreciable amounts of benzaldehyde, but other reactions predominated. No tertiary amine was recovered in either case.[9] Although it was thus not possible to attain the original objective of comparing the susceptibility to nitrosative dealkylation under controlled conditions as a function of substituent effects on the aniline ring, it is evident from the inertness of the *p*-nitro member, which must be by far the weakest base, that a qualitative parallel exists between susceptibility and base strength.

To determine whether the unshared electron pair of the tertiary amine free base is necessary for nitrosative dealkylation, the quaternary derivative, methyltribenzylammonium nitrate was subjected to the usual nitrosating treatment at 95° for 45 min. The original compound was recovered in 70% yield, and no aldehyde or nitrosamine could be detected. A similar experiment with tribenzylamine N-oxide, however, did result in cleavage to benzaldehyde and dibenzylnitrosamine; these are the products obtained from tribenzylamine itself however.

Quinuclidine was subjected to the same reaction conditions to determine whether resistance to double-bond formation at the bridgehead nitrogen would interfere with dealkylation. The starting material was recovered in 92% yield.

The effect of essentially electronic factors was investigated by means of a group of tribenzylamines each bearing a *para* substituent on one benzyl group. In an orienting series of experiments, the mixed aldehydes and the mixed nitrosamines were isolated by distillation. The composition of the aldehyde mixture was then determined by fractional distillation and by vapor phase chromatography; the nitrosamines were converted to secondary amines by treatment with urea and alcoholic hydrochloric acid, and then fractionated. The results are collected in Table I. The effect of temperature was examined by experiments covering a 30° range. For these experiments, the *p*-nitro derivative was not used, owing to its incomplete reaction. Only the aldehydes were used to determine product ratios in this group of experiments, since they were obtained in higher yields than the amines. The compositions were determined by vpc, standardized against known mixtures; the results are collected in Table II.

The effect of α substitution on the nitrosative cleavage of tribenzylamine was investigated with the α-methyl, α-ethyl, and α-carboethoxy derivatives. For comparison, benzyldiethylamine and its α-methylbenzyl and α-carboethoxybenzyl analogs were also studied, along with dibenzylhexahydrobenzylamine. The product ratios were determined either by distillation (with or without hydrolysis of the nitrosamines) or by vpc, as feasibility and reliability indicated. Inasmuch as the reactions were in some cases far from complete, and in others were accompanied by secondary reactions, and some of the products underwent partial decomposition during distillation or chromatography, the ratios determined are more qualitative than quantitative; however we believe the yields of products isolated to provide reliable minima. The results are collected in Table III.

Tribenzylamine-α,α-d_2 was examined for the appearance of an isotope effect in nitrosative cleavage. The required substance was prepared by reduction of N,N-dibenzylbenzamide with lithium aluminum deuteride; the percentage of deuteration determined by the falling-drop method of Keston,[10a] was 88.5%. The benzaldehyde obtained by nitrosative cleavage at 95° was examined for deuterium content by the infrared method of Wiberg;[10b] it contained 7.8% of deuteriobenzaldehyde. The dibenzylnitrosamine was examined by means of its integrated nmr spectrum; about 7% of it was deuterium free. The isotope effect, k_H/k_D, was calculated from these data using a statistical effect of 1:3; the value obtained from the benzaldehyde analysis, $0.333 \times 88.5/7.8 = 3.78$, is considered to be the more reliable.

Brief attention was also given to the closely related reactions of nitrosyl chloride and nitrosyl fluoroborate with tertiary amines in anhydroxylic medium. Jones and Whalen[11] have reported that nitrosyl chloride and trimethylamine form an addition compound at low temperatures, and that it decomposes below 0° to give off nitric oxide and leave a colorless solid, from which trimethylamine and dimethylamine salts could be obtained. We obtained analogous results with tribenzylamine, which gave as a major product tribenzylamine hydrochloride, together with substantial quantities of another salt partially separable from the former by solution in benzene. The more soluble salt was readily

Table I. Product Ratios from the Nitrosative Cleavage of Monosubstituted Tribenzylamines, $RC_6H_4CH_2N(CH_2C_6H_5)_2$, at 90–95°

R	Total aldehydes, %	Mole ratio, C_6H_5CHO/RC_6H_4CHO	Total secondary amines, %	Mole ratio, $C_6H_5CH_2NHCH_2C_6H_4R/(C_6H_5CH_2)_2NH$
p-CH_3O	82	1.468[a] 1.758[b]	69	1.95
m-CH_3	86	2.12[a] 1.95[b]	59	1.95
p-Cl	81	2.12[a]	61	2.1
p-NO_2	39[c]	2.64[a]	53[c]	2.5

[a] By fractional distillation. [b] By vpc. [c] Not corrected for an appreciable amount of unreacted starting material.

Table II. Effect of Temperature on Product Ratios from Monosubstituted Tribenzylamines, $RC_6H_4CH_2N(CH_2C_6H_5)_2$

R	C_6H_5CHO/RC_6H_4CHO 62.8°	81.3°	93.8°
p-CH_3O	1.35	1.61	1.88
m-CH_3	1.71	2.00	1.94
p-Cl	2.11	2.22	1.88

(9) Other examples of competition of ring substitution with nitrosative cleavage of dialkylanilines have been reported by G. P. Crowley, G. J. G. Milton, T. H. Reade, and W. M. Todd, *J. Chem. Soc.*, 1286 (1940).

(10) (a) A. S. Keston, D. Rittenberg, and R. Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1938); (b) K. Wiberg, *J. Am. Chem. Soc.*, **76**, 5371 (1954).

(11) L. W. Jones and H. F. Whalen, *ibid.*, **47**, 1343 (1925).

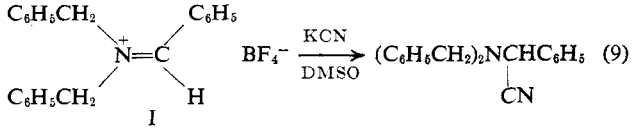
Table III. Nitrosative Cleavage of Various Tertiary Amines $R_2CHN(CHR_2')_2$

R_2CH	$R_2'CH$	Products isolated, %[a]	Cleavage ratio,[b] $R_2CH/R_2'CH$
$C_6H_5CH(COOEt)$	$C_6H_5CH_2$	C_6H_5CHO 50	<1/99[c]
$C_6H_5CH(Et)$	$C_6H_5CH_2$	C_6H_5CHO, 80; C_6H_5COEt, 1.7; $R_2CHNHCHR_2'$, 82	2/98
$C_6H_5CH(CH_3)$	$C_6H_5CH_2$	(C_6H_5CHO, $C_6H_5COCH_3$)	8/92[d]
$(CH_2)_5CHCH_2$	$C_6H_5CH_2$	C_6H_5CHO, 50; $(CH_2)_5$-$CHNHCHC_6H_5$	<1/100
$C_6H_5CH(COOEt)$	Et	R_2CO, 16.4; $R_2CHN(Et)NO$, 57	22/78
$C_6H_5CH(CH_3)$	Et	R_2CO, 3; $R_2CHN(Et)NO$, 38	8/92
$C_6H_5CH_2$	Et	C_6H_5CHO, 16; $C_6H_5CH_2N(Et)NO$, 57.5	21/79

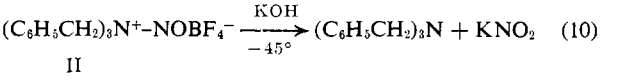
[a] Other products, particularly acetaldehyde and diethylnitrosamine, were occasionally isolated, but are not reported here because the yields were not felt to be sufficiently reliable. [b] Normalized to a basis of 100. [c] Vpc analysis showed only benzaldehyde. [d] Vpc analysis.

hydrolyzed by hot water to give dibenzylamine hydrochloride and benzaldehyde, but unfortunately could not be obtained pure. Further experiments were carried out using nitrosyl fluoroborate instead, in the unrequited hope of obtaining a more readily purified product.

Nitrosyl fluoroborate suspended in chloroform reacted with tribenzylamine at −10° to give chloroform-soluble products, which were precipitated as a mixture of colorless solids by addition of petroleum ether. Hydrolysis with hot water produced tribenzylamine and dibenzylamine hydrochlorides and benzaldehyde. The infrared spectrum of the solid mixture was distinguished by absorptions at 3200 and 1650 cm^{-1}, and the absence of absorption at 3400 cm^{-1}, where dibenzylamine fluoroborate absorbs. On standing in moist air, the solid slowly lost the 1650 band, and one at 3400 cm^{-1} developed. These features agree with the presence of tribenzylammonium fluoroborate (infrared at 3200 cm^{-1}) and N,N-dibenzylbenzaldimmonium fluoroborate (I) (infrared at 1650 cm^{-1} attributable to $C{=}N^+$); moisture would convert the latter compound to dibenzylammonium fluoroborate (*cf.* eq 5), thus accounting for the changes in the spectrum. The nmr spectrum of a chloroform solution of the solid mixture confirmed these deductions. In addition to the aromatic proton signals, there was a singlet at τ 0.50, attributable to the aldimmonium hydrogen, a doublet at τ 5.6, and two equal singlets, at τ 4.78 and 4.61. The doublet, whose area showed no whole-number relationship to any of the singlets, is attributed to tribenzylammonium fluoroborate, which gives an identical signal. The two singlets can be attributed to the *cis*- and *trans*-benzyl group methylenes of the immonium salt. The relative areas of the two singlets and the doublet indicated about 40% of immonium salt in the mixture. The identity of I in the product was further confirmed by hydrolysis, which gave benzaldehyde (18%) and a mixture of dibenzylamine and tribenzylamine in a ratio of 1:1.8. Furthermore, treating the mixture with potassium cyanide in dimethyl sulfoxide gave α-cyanotribenzylamine in good yield (eq 9).

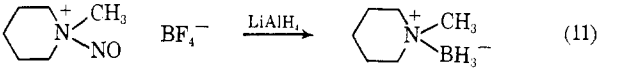


The reaction of nitrosyl fluoroborate and tribenzylamine gave rise to a different initial product when carried out at −55°; a red substance, insoluble in chloroform below about −20°, appeared. At temperatures of −20° or above, the red substance slowly lost its color and evolved gas; examination of the residue showed it to be a mixture of salts similar to what had been obtained directly at higher temperatures. Treatment of the red precipitate with alcoholic potassium hydroxide at −45° produced tribenzylamine and potassium nitrite, in an approximately 1:1 ratio, and no dibenzylamine, which shows that formation of immonium salt had not yet taken place. The red compound is thus presumably N-nitrosotribenzylammonium fluoroborate (II). The possibility that it



might be merely a mixture of the reactants is rendered unlikely by the fact that tribenzylamine is soluble in chloroform under the conditions of the experiments.

Attempts to reduce II to a quaternary hydrazinium salt with lithium aluminum hydride invariable brought about N–N cleavage, even at low temperatures, and only tribenzylamine was obtained. Reduction was also explored using the N-methylpiperidine–nitrosyl fluoroborate adduct, but the only reduction product that could be obtained was N-methylpiperidine–borane (eq 11). Treatment of the corresponding quaternary



hydrazinium salt, N-methyl-N,N-pentamethylenehydrazinium fluoroborate, with lithium aluminum hydride gave the same product.

Discussion

In addition to the previously proposed mechanisms cited at the beginning of this paper, one more deserves consideration. It is bimolecular hydride abstraction from an α carbon by nitrosonium ion, giving nitroxyl and the same immonium species that appears in eq 4 and 5. The stoichiometry that we have determined, and particularly the formation of nitrous oxide, eliminates only the cation radical mechanism (eq 2 and 3). The implications of the remaining evidence will therefore be discussed in terms of the three other mechanisms.

The over-all implication of the various reports of nitrosative cleavage over the past century is that a rela-

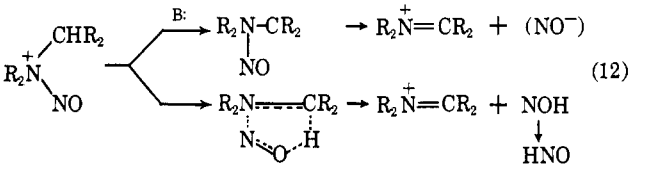
tively weakly acid solution is required. In fact, the failure of Heintz[3] to observe any cleavage whatsoever may be attributed to the fact that he used concentrated hydrochloric acid as his medium, in contrast to Guether,[2] whose work he purported to repeat. Furthermore, the reaction generally requires mild warming for best results, and thus may be regarded as intrinsically slower than the reaction of primary and secondary amines with nitrous acid (however, even some primary amines require heating for reaction). It is this difference in reactivity, although it is not sharp, together with the customary use of fairly strong hydrochloric acid, that is presumably responsible for such reliability as there is in the use of nitrous acid as a test to distinguish among the classes of amines.

It appears that the function of acid in nitrosative cleavage is to generate the required nitrosating species,[12] but that reaction is retarded or prevented insofar as the amine is at the same time converted to its conjugate acid. This view is strongly supported by the fact that the quaternary compound, methyltribenzylammonium nitrate, did not undergo cleavage. A related experiment directed to the same point, the exposure of tribenzylamine oxide to nitrosative cleavage conditions, was not of value, for it was found that nitrous acid also achieves reduction (presumably before C–N cleavage), and gives the same products as obtained from the tertiary amine. The apparent necessity for an unshared electron pair weighs against the bimolecular hydride abstraction mechanism, but it is not proof, inasmuch as the positive charge on an ammonium ion would assuredly hinder the availability of hydride to an approaching cation such as nitrosonium ion. The experiments with base-weakening substituents on dibenzylanilines however, particularly the inertness of N,N-dibenzyl-*p*-nitroaniline, are more forceful. The electronic effects of the nitro group should be relatively small on the benzylic hydrogens, whereas its effect on the availability of the unshared electron pair on nitrogen is large, as revealed by the base strength of aniline (pK_a = 4.59) compared to that of *p*-nitroaniline (pK_a = 1). The formation of the N-nitrosoammonium ion, a feature of both the elimination mechanism and the dealkylation mechanism, would be strongly retarded by such base-weakening substitution.

The inertness of quinuclidine, which is a respectably strong base (pK_a = 10.58) may be taken as evidence that a C=N double bond, which could not form readily to a bridgehead atom, may be involved in nitrosative cleavage. The nucleophilic dealkylation path, however, would also be denied by the cage structure, so that this experiment really casts doubt only on the cation radical mechanism.

The effects of ring substitution on product selection in tribenzylamines (Tables I and II) show that susceptibility to electronic effects is low, and that electron withdrawal retards removal of the group involved. The results can be correlated by the Hammett equation in the form log (ArCHO/0.5C_6H_5CHO) = $\rho\sigma$, for the results are presumably determined by the relative rates of cleavage involving the respective groups. The values of ρ are −0.39 at 62.8°, −0.25 at 81.3°, −0.14 at 93.8°, and −0.17 for the pilot experiments at 90–95°. A plot of these values against the reciprocal temperature gives a straight line obeying the equation $\rho = -0.08/T + 2$; an isokinetic temperature of 117° is indicated. It is probably unwise to read deep meaning into these figures, in view of the limitations of the data and the proximity to the isokinetic temperature, but it is safe to say that the results can be reconciled qualitatively with all three remaining mechanisms. The negative value of ρ is consistent both with dealkylation by an SN1 process (involving formation of benzyl cations) and with removal of a benzylic hydrogen with its electron pair (bimolecular or intramolecular). The pronounced deuterium isotope effect, however, virtually eliminates nucleophilic dealkylation mechanisms (SN1 or SN2), for product selection would be subject only to a secondary, not a primary, deuterium isotope effect. Primary isotope effects of slightly lower magnitude (1.8 to 2.2) have, indeed, been observed[13] in the pyrolysis of xanthate and acetate esters to form olefins, reactions that are well established as examples of *cis* elimination.

It should be noted at this point that the elimination mechanism may be intramolecular, involving a cyclic transition state, which implies a *cis* geometry for the process, or it may be bimolecular, involving an external base (or simultaneous proton acceptor–donor) to



(12)

remove a proton from an α carbon (eq 12). The negative value of the Hammett reaction constant with substituted tribenzylamines is good evidence against bimolecular base-catalyzed elimination, which requires a protonic α hydrogen, and therefore implies the intramolecular process and the geometrical consequences of *cis* elimination. The experiments with α-substituted tertiary amines (Table III) are directed to this point. Even though the significance of the results is limited by the lack of good material balance, the essential point is inescapable, that the electronic nature of the α substituent is of minor significance compared with its steric effect. For example, the overwhelming formation of benzaldehyde from both α-ethyl- and α-carboethoxytribenzylamine is not reconcilable with the opposite electronic influences of these two substituents.

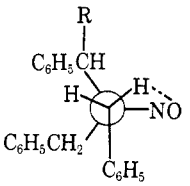
All of the observations of the effects of α substituents can be correlated on the basis of nonbonded interactions in a cyclic transition state. This may be done by means of Newman projections (III and IV). Rotation of an unsubstituted benzyl group into position for *cis* elimination of a hydrogen and the nitroso group brings about only one site of eclipsing not involving hydrogen; rotation of an α-substituted benzyl group into the position for elimination, on the other hand, sets up two sites where eclipsing can be expected to be accompanied by steric interference. It is thus implied that the unsubstituted benzyl groups will be preferentially cleavaged from α-substituted tribenzylamines, in agreement with all the examples investigated. By precisely analogous reasoning, it can be predicted that (apart from statistical effects) hexahydrobenzyldibenzylamine will undergo preferential cleavage of a benzyl group,

(12) T. A. Turney and G. A. Wright, *Chem. Rev.*, **59**, 497 (1959).

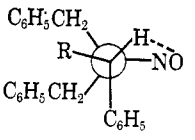
(13) C. H. Depuy and R. W. King, *ibid.*, **60**, 431 (1960).

whereas benzyldiethylamine will undergo preferential cleavage of an ethyl group, notwithstanding the fact that the situations are electronically similar, in each case an alkyl group being pitted against benzyl. It is only necessary to make the reasonable assumption that the steric requirements of a benzyl group are less than those of hexahydrobenzyl, but larger than those of ethyl. The results reported in Table III are in accord with these deductions.

We conclude, therefore, that the process represented by eq 4–6, with *cis* elimination of nitroxyl in the product-determining step, best fits the available facts about nitrosative cleavage of tertiary amines. It should be noted, however, that N-methyl-N-ethyl-*p*-nitroaniline has been reported[9] to undergo nitrosative cleavage of the ethyl group preferentially, which is the opposite of the expectation on the basis of the foregoing considerations. On the other hand, this result was obtained by means of



III



IV

differential melting point determination of the mixed neutral products of the reaction; since no evidence was presented that the mixtures consisted wholly of the assumed pair of nitrosamines, the analysis may have been in error.

The experiments with nitrosyl chloride and fluoroborate show that the products of the reaction of these nitrosating reagents with tertiary amines are different from those of aqueous nitrous acid. The reactions may, nevertheless, be considered analogous, for the differences are precisely those that would be anticipated to result from the differences in the reaction media. In a nonhydrolytic medium, as used with the nitrosyl compounds, the reaction cannot go beyond the elimination stage (eq 4 and 12), and the immonium salt intermediate deduced for the aqueous nitrosation reactions can actually be isolated. The unstable addition compounds obtained with the nitrosyl compounds at low temperatures have the characteristics to be expected of the postulated N-nitrosotrialkylammonium salts, and their saponification to tertiary amine and nitrite in particular lends strong support to such a formulation.

The concomitant formation of tertiary amine salt, together with nitric oxide instead of nitrous oxide, when nitrosyl compounds are used as nitrosating agents, may be accounted for by reaction of the nitrosyl compounds with nitroxyl (eq 13 and 14); only a very small amount of free nitrosyl compound need remain with the nitrosammonium salt (as a result of either mechanical retention or dissociation of the salt) to provide such a path, for it would be regenerated by eq 15. The resulting stoichiometry, by which tertiary amine salt and immonium salt are produced in equimolar quantities (eq 16) would be consistent with the observed presence of an excess of tribenzylamine in the products if it can be assumed that decomposition of the nitrosammonium intermediate was not complete in the experiments with nitrosyl fluoroborate. Equation 16 is also consistent with the proportion of nitric oxide

$$R_3N^+\text{–}NOX^- \longrightarrow HNO + \text{immonium salt} \quad (13)$$

$$HNO + NO^+X^- \longrightarrow 2NO + HX \quad (14)$$

$$R_3N^+\text{–}NOX^- + HX \longrightarrow R_3NH^+X^- + NO^+X^- \quad (15)$$

$$2R_2N\text{–}CHR_2' + 2NOX \longrightarrow R_2\overset{+}{N}H\text{–}CHR_2'X^- + R_2N^+{=}CR_2'X^- + 2NO \quad (16)$$

obtained by Jones and Whalen[11] from the reaction of nitrosyl chloride with trimethylamine.

Experimental Section[14]

Secondary Amines. The general preparative method involved the dropwise addition of 0.2 mole of aldehyde over a 1.5-hr period to a cold, stirred solution of 0.2 mole of the appropriate primary amine in 50 ml of absolute ethanol. This solution was then added to 0.2 g of prereduced platinum oxide and hydrogenated at ~3 atm. Dibenzylamine[15] and its *p*-methoxy[16] and *p*-chloro[17] derivatives, N-(cyclohexanemethyl)benzylamine,[18] N-benzyl-*p*-chloroaniline,[19] N-benzyl-*p*-anisidine,[20] and N-benzyl-*p*-toluidine[21] are known compounds. *m*-Methyldibenzylamine, bp 118° (0.2 mm), was obtained as a colorless oil in 88% yield.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.38; H, 8.12; N, 6.64. Found: C, 85.50; H, 8.20; N, 6.76.

N-Benzyl-1-phenylpropylamine. A solution of 58.5 g (0.3 mole) of benzylidenebenzylamine[22] in 250 ml of dry ether was added dropwise to a stirred solution of ethylmagnesium bromide which had been prepared from 14.4 g (0.6 g-atom) of magnesium and 66 g (0.6 mole) of ethyl bromide. A mildly exothermic reaction ensued, and the mixture was heated under reflux overnight. After treatment of the cooled mixture with a saturated solution of ammonium chloride, filtration from salts, and drying over potassium carbonate, the ether was removed and the amine was distilled at 118–120° (0.75 mm) to give 27 g (0.12 mole, 40%) of pure N-benzyl-1-phenylpropylamine. (The hydrochloride melted at 171°.)

Anal. Calcd for $C_{16}H_{18}N$: C, 85.40; H, 8.45; N, 6.17. Found: C, 85.59, H, 8.53; N, 6.17.

Tertiary Amines. Most of the tertiary amines were prepared by procedures analogous to the preparation of 4-methoxytribenzylamine, described here. Benzyl bromide (30 g, 0.15 mole) was added to a stirred mixture of 34 g (0.15 mole) of 4-methoxydibenzylamine, 45 ml of glycerol, and 16 g of sodium carbonate. The flask was flushed with nitrogen, and the mixture was heated with stirring at 150° for 24 hr. The cooled reaction mixture was poured into 250 ml of water and extracted with three 100-ml portions of ether. The ether was removed from the combined, dried extracts, and the residual oil was distilled to give 40 g (0.126 mole, 84%) of 4-methoxytribenzylamine, bp 190° (0.4 mm). The results for the other tertiary amines are collected in Table IV.

N,N-Dibenzyl-4-chloroaniline. A mixture of 127 g (1 mole) of 4-chloroaniline, 125 g of sodium carbonate, 150 ml of glycerol, and 253 g (2 moles) of benzyl chloride was heated at 150° with stirring under nitrogen for 18 hr, before being cooled and poured into 500 ml of water. The aqueous mixture was extracted with three 350-ml portions of ether, and the ether solution was dried over anhydrous sodium sulfate, filtered, and stripped of ether to give an oil, which solidified to a white solid. Recrystallization from ethanol gave 202 g (66%) of N,N-dibenzyl-4-chloroaniline, mp 101–103°.

Anal. Calcd for $C_{20}H_{18}ClN$: C, 77.76; H, 5.90; N, 4.41. Found: C, 77.92; H, 6.01; N, 4.50.

N,N-Dibenzyl-4-methoxy-2-nitroaniline, prepared similarly from benzyl bromide and 4-methoxy-2-nitroaniline,[23] was obtained as

(14) Infrared spectra were determined on a Perkin-Elmer Infracord. Nmr spectra were determined with a Varian Associates A-60 instrument, and are referred internally to tetramethylsilane. Microanalyses are by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points are uncorrected.
(15) K. Kindler, *Ann.*, **485**, 113 (1931).
(16) H. R. Snyder and J. R. Demuth, *J. Am. Chem. Soc.*, **78**, 1981 (1956).
(17) J. von Braun, M. Kuhn, and J. Weismantel, *Ann.*, **449**, 249 (1926).
(18) G. Costorina, *Farmaco* (Pavia), *Ed., Sci.*, **9**, 218 (1954).
(19) D. H. Peacock, *J. Chem. Soc.*, **125**, 1979 (1924).
(20) E. Fröhlich and E. Wedekind, *Ber.*, **40**, 1010 (1906).
(21) L. Kohler, *Ann.*, **241**, 359 (1887).
(22) R. E. Juday and H. Adkins, *J. Am. Chem. Soc.*, **77**, 4559 (1955).
(23) P. E. Fanta and D. S. Tarbell, *Org. Syn.*, **25**, 78 (1945).

Table IV. Tertiary Amines

Product, tertiary amine	Alkyl halide	Source, secondary amine	Mp or bp (mm), °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Yield, %
4-Methoxytribenzylamine[a]	Benzyl bromide	4-Methoxydibenzylamine	190 (0.4)	65.24	5.97	3.46	65.18	6.20	3.59	84
4-Chlorotribenzylamine[b]	Benzyl bromide	4-Chlorodibenzylamine	160 (0.3)	61.59	5.17	3.42	61.63	5.24	3.59	80
3-Methyltribenzylamine[c]	Benzyl bromide	3-Methyldibenzylamine	171 (0.1)	67.92	6.22	3.60	68.09	6.35	3.60	84
4-Nitrotribenzylamine	4-Nitrobenzyl bromide	Dibenzylamine	55–56	75.97	6.07	8.44	75.82	6.01	8.45	80
N-(Cyclohexylmethyl)-dibenzylamine	Benzyl bromide	N-(Cyclohexylmethyl)benzylamine	47–50	86.08	9.29		86.19	9.25		71
N,N-Dibenzyl-α-phenylpropylamine	Benzyl chloride	N-Benzyl-α-phenylpropylamine	144 (0.06)	87.69	8.00	4.45	87.55	8.11	4.48	
α-Carbethoxytribenzylamine	Ethyl α-bromophenylacetate	Dibenzylamine	175 (0.075)	80.20	7.02	3.90	79.91	6.88	3.93	66

[a–c] Analyzed as HBF_4 salts; mp *a*, 150–151°; *b*, 173–174°; *c*, 179–181°.

bright yellow crystals from ether, mp 104–105°. N,N-Dibenzyl-*p*-anisidine,[24] mp 81–82°, was prepared similarly.

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.47; H, 5.79; N. 8.05. Found: C, 72.36; H, 5.98; N, 8.05.

α-Cyanotribenzylamine. A solution of 15.9 g (0.15 mole) of benzaldehyde and 50 ml of glacial acetic acid was stirred while 30 g (0.15 mole) of dibenzylamine was added. After the exothermic reaction had subsided, 10 g (0.15 mole) of potassium cyanide dissolved in 20 ml of water was added dropwise. Upon cooling, an oil separated and solidified; it was recrystallized from ethanol to give 46.5 g (97%) of α-cyanotribenzylamine, mp 103–104°. The infrared spectrum (Nujol mull) showed no absorption in the region of the C≡N stretching frequency, but such behavior is not uncommon for α-amino and α-hydroxy nitriles.

Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.69; H, 6.46; N, 8.78. Found: C, 84.74; H, 6.54; N, 8.81.

The General Procedure for the Nitrosation of Tertiary Amines in Aqueous Acetic Acid. The amine (0.1 mole) was dissolved in 500 ml of 60% aqueous acetic acid buffered to pH 4–5 with 68 g of sodium acetate. The mixture was stirred and heated on the steam bath to a temperature of approximately 90°. At this point the dropwise addition of 69 g (1 mole) of sodium nitrite dissolved in 100 ml of water was commenced and allowed to continue with heating over a period of about 45 min. After heating for an additional 2 hr, the mixture was cooled, poured into 200 ml of cold water, and extracted with three 200-ml portions of ether. The combined ether extracts were washed with 10% potassium carbonate until the aqueous layer was basic, then with saturated salt solution, and finally were dried over anhydrous sodium sulfate.

Assay of the Nitrosation Mixtures. The ethereal mixture of products from the nitrosation was concentrated, and a small sample was taken from vpc analysis. The remaining solution was completely stripped of ether, and the carbonyl products were fractionally distilled at aspirator pressure through an efficient column. The carbonyl products were weighed and characterized by a comparison of their infrared spectra and the melting points of their 2,4-dinitrophenylhydrazone or semicarbazone derivatives with those of the authentic compounds.

The distillation residue containing the nitrosamine portion of the reaction mixture was refluxed for 60 hr in 300 ml of ethanol containing 12 g of urea and 50 ml of concentrated hydrochloric acid. The alcohol was removed (aspirator), and the residual salts were basified with ammonium hydroxide. The mixture was extracted with three 125-ml portions of ether, and the combined extracts were washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. The ether was stripped off, and the oily mixture of secondary amines was fractionally distilled under reduced pressure. The amines were weighed and then converted to their hydrochlorides for characterization.

The results of the assay are shown in Table II. The low vapor pressure and high polarity of the nitrosamines did not allow their analysis by vpc. The vpc analysis of the carbonyl compounds was carried out with a Barber-Coleman Model 8000-2600 J 5 gas chromatograph (Sr^{90} ionization detector) with a 6-ft Ucon oil-on-Firebrick column at a temperature of 145°. Retention times were compared with authentic samples and integration was performed with the aid of a planimeter.

Isolation of the Amines from the Nitrosation of 4-Methoxytribenzylamine. When it was found that the treatment of 4-methoxydibenzylnitrosamine with alcoholic hydrochloric acid brought about partial cleavage of the methoxyl group, the following procedure was adopted. The aldehydes were distilled off at reduced pressure and set aside. The nitrosamines were dissolved in 400 ml of 95% ethanol and reduced by the portionwise addition of 600 g of 2.5% sodium amalgam and 40 g of acetic acid over 1 hr. The mercury was removed and the alcohol stripped off at reduced pressure. The resulting residue was taken up in ammonium hydroxide and extracted with several portions of ether. The combined ether extracts were dried over anhydrous potassium carbonate, the ether was evaporated, and the mixture of amines was fractionated.

Treatment of Tribenzylamine with a Limited Amount of Nitrous Acid. Tribenzylamine[25] (28 g, 0.1 mole) was treated with 7 g (0.1 mole) of sodium nitrite by the general procedure. The crude product mixture was distilled to give a small quantity of benzaldehyde and 8.49 g (38%) of dibenzylnitrosamine, bp 140–143° (0.1 mm), mp 59–60° (lit.[26] mp 59°). No other material distilled. The pot residue was taken up in ethanol and recrystallized to give 14.5 g (51.6%) of tribenzylamine, mp 90–91° (reported 90°). The material balance on the amines was 89.6%.

Nitrosation of 4-Nitrotribenzylamine. After the standard nitrosation procedures, the ether was distilled off and the benzaldehyde (3 g, 0.028 mole) distilled at 70–80° (17 mm). The remaining viscous oil was sublimed at 0.5 mm to give *p*-nitrobenzaldehyde (1.62 g, 0.011 mole). The residue was refluxed with 50 ml of concentrated hydrochloric acid and 12 g of urea in 250 ml of ethanol for 36 hr. The alcohol was removed (aspirator), and the residue was treated with excess ammonium hydroxide. The mixture was extracted with ether, and the extracts were dried over anhydrous sodium sulfate. The ether was evaporated, and the resulting oil was distilled at 140° (0.7 mm) to give dibenzylamine (2.96 g, 0.015 mole). The residue was dissolved in anhydrous ether, and hydrogen chloride was bubbled through until precipitation ceased. The precipitate (10.48 g, 0.038 mole) was filtered off, mp 244–248°, undepressed by an authentic sample of 4-nitrodibenzylamine hydrochloride. The filtrate was treated with more hydrogen chloride, and another precipitate formed. This material (6.06 g, 0.0165 mole) melted at 190–194°, undepressed by authentic 4-nitrotribenzylamine hydrochloride.

Nitrosation at Different Temperatures. The amines nitrosated were 3-methyl-, 4-chloro-, and 4-methoxytribenzylamine. A stock solution of the solvent for the experiment was prepared by mixing 68 g of sodium acetate, 300 ml of glacial acetic acid, and 200 ml of water. Each nitrosation was carried out at 62.8, 81.3, and 93.8° in a constant-temperature bath. A mixture of 0.01 mole of the

(24) D. P. Clark, Jr., U. S. Patent 2,454,034; *Chem. Abstr.*, **43**, 1178*b* (1949).

(25) A. T. Mason, *J. Chem. Soc.*, **63**, 1314 (1893).

(26) T. Curtius and H. Franzen, *Ber.*, **34**, 552 (1901).

amine and 50 ml of solvent was stirred together for 1 hr prior to the addition of 10 ml of 7.7 *M* sodium nitrite solution, which was withdrawn with a syringe from a flask immersed in the constant temperature bath. After 1 hr the reaction mixture was poured into 150 ml of water and extracted with three 30-ml portions of ether, which were combined and washed with 10% potassium carbonate solution, and then dried over anhydrous sodium sulfate.

The extracts were analyzed for aldehydes by vapor phase chromatography; analysis of known mixtures showed that the method was correct to within 1%. (Known mixtures of benzaldehyde and the substituted aldehyde gave the following analyses: *p*-chloro, molar ratio (mr) 1.65, area ratio (ar) 1.58; 3-methyl, mr 0.578, ar 0.576; 4-methoxy, mr 0.818, ar 0.830.) The area ratio of the vpc peaks for a given run divided into a statistical factor of two gives k_2/k_1, values for which are given in Table II.

Nitrosation of N-(Cyclohexylmethyl)dibenzylamine. N-(Cyclohexylmethyl)dibenzylamine (21 g, 0.075 mole) was nitrosated by the general procedure. Analysis of the product mixture by vpc showed benzaldehyde to be the only carbonyl-containing product. Distillation of the reaction mixture produced benzaldehyde (4 g, 50%) and 14 g of a yellow oil, bp 125° (0.02 mm), presumed to be N-(cyclohexylmethyl)benzylnitrosamine. The oil was treated with ethanolic hydrochloric acid in the manner described previously. A single substance, distilling at 103° (0.2 mm), was obtained; its infrared spectrum and the melting point of the benzenesulfonamide (75°) were identical with those from N-(cyclohexylmethyl)benzylamine.

Nitrosation of N,N-Dibenzyl-1-phenylpropylamine. N,N-Dibenzyl-1-phenylpropylamine (31 g, 0.1 mole) was nitrosated by the general procedure. Analysis by vpc showed a ratio of 1.7% benzophenone to 98.3% benzaldehyde. Distillation produced only benzaldehyde (8.1 g, 80%); after the denitrosation treatment, N-benzyl-1-phenylpropylamine (19 g, 82%) was the only nitrogen-containing product isolated (identified by infrared comparison).

Nitrosation of N,N-Diethyl-1-phenylethylamine. A mixture of 35 g (0.2 mole) of N,N-diethyl-1-phenylethylamine[27] and 200 ml of buffered 60% acetic acid solution was heated on a steam bath with stirring while 110 ml of 7.7 *M* sodium nitrate solution was added over a 45-min period; an ice-cooled trap containing ethanol was connected to the top of the reflux condenser on the apparatus. The mixture was stirred for an additional 2 hr, cooled, poured into 300 ml of water, and extracted with three 100-ml portions of chloroform, which were combined and washed with water, dilute sodium hydroxide solution, and saturated salt solution. After drying over anhydrous sodium sulfate, the chloroform was stripped off, and the residue was taken up in dry *n*-butyl ether. A stream of anhydrous hydrogen chloride was bubbled through while the solution was heated on the steam bath. A precipitate formed gradually and was removed by filtration after 30 min. The filtrate was washed with dilute base, dried over sodium sulfate, and distilled to give in addition to *n*-butyl ether, 1 g (3%) of acetophenone, which gave a 2,4-dinitrophenylhydrazone, mp 248° (lit.[28] mp 249–250°).

The precipitate was treated with aqueous base and extracted with ether. Distillation of the dried extracts gave a low-boiling fraction, which when treated with picric acid produced a picrate melting at 154°, undepressed by authentic diethylammonium picrate. Further distillation gave 6 g (18.5%) of N-ethyl-1-phenylethylamine, bp 85–90° (15 mm) (hydrochloride mp 201°, undepressed by an authentic sample).

The ethanol in the trap gave a small amount of acetaldehyde 2,4-dinitrophenylhydrazone, mp 145–146° (undepressed by an authentic sample).

In a separate experiment where the work-up was carried out as described in the general procedure, 0.0761 mole (38%) of N-ethyl-1-phenylethylamine was obtained from 0.2 mole of N,N-diethyl-1-phenylethylamine.

Nitrosation of N,N-Dibenzyl-4-chloroaniline. N,N-Dibenzyl-4-chloroaniline (32 g, 0.1 mole) was nitrosated by the general procedure, and the drowned reaction mixture was extracted with three 100-ml portions of chloroform. The combined extracts were washed with water, 10% potassium carbonate solution, and saturated salt solution, dried over anhydrous sodium sulfate, and distilled to give 4.2 g (42%) of benzaldehyde, bp 70–75° (20 mm).

The residue from the distillation was poured while hot into 95% ethanol and cooled to give yellow crystals of N-benzyl-N-nitroso-4-chloroaniline. This material (15 g, 62%), after drying had mp 57°, alone or mixed with authentic material.[29]

In an experiment carried out at 50–60°, about 60% of the starting amine was isolated unchanged in addition to the nitrosation products.

Nitrosation of N,N-Dibenzyl-*p*-anisidine. The drowned reaction mixture from the nitrosation of 30 g of N,N-dibenzyl-*p*-anisidine (0.1 mole) was extracted with three 200-ml portions of chloroform. The combined extracts were washed with water, 10% potassium carbonate solution, and saturated salt solution, dried over sodium sulfate, and evaporated; the oily residue was divided into two equal portions.

The first portion gave only benzaldehyde (2 g), bp 70–75° (20 mm), on distillation, identified by its infrared spectrum and its 2,4-dinitrophenylhydrazone, mp 235–237°, undepressed by an authentic sample.

The second portion was taken up in ethanol and cooled to give yellow crystals (13 g), melting range 70–98°. Chromatography of a 5-g sample on 200 g of alumina gave two fractions: the first eluted with 10% benzene–petroleum ether mixture, consisted of 3.28 g (49.5%) of N,N-dibenzyl-4-methoxy-2-nitroaniline, mp 104–105°, undepressed by an authentic sample; the second, eluted with benzene, consisted of 1.70 g (37%) of N-nitroso-N-benzyl-*p*-anisidine, mp 77–78°, undepressed by authentic sample.[30]

In an experiment carried out below 70°, N,N-dibenzyl-2-nitro-4-methoxyaniline (21 g, 61%) was the only product obtained from 30 g of the starting amine.

Nitrosation of N,N-Dibenzyl-*p*-toluidine. N,N-Dibenzyl-*p*-toluidine[31] (28 g, 0.1 mole) was nitrosated by the general procedure and worked up as described for N,N-dibenzyl-*p*-anisidine. Benzaldehyde could be isolated from one portion of product mixture; the second portion, which could not be induced to crystallize, was chromatographed on alumina to give three fractions. The first and major fraction, eluted with 20% benzene–petroleum ether, was a dark red oil (3.5 g), which was distilled to give N-benzyl-*p*-toluidine (1.08 g), bp 116° (0.8 mm), identical with an authentic sample.[21] The distillation residue would not crystallize.

The second fraction (3 g), eluted with 50% benzene–petroleum ether, consisted of N-nitroso-N-benzyl-*p*-toluidine, mp 50–52°, identical with an authentic sample.[21]

The third fraction, eluted with 10% ether–benzene, gave 220 mg of a crystalline compound, mp 107–108°, whose analysis suggested the empirical formula $C_{14}H_{13}N_3$. Its infrared spectrum showed no N–H absorption, but the ultraviolet spectrum (in methanol) showed two peaks [λ_{max} 2575 (ϵ 7.81 × 10³) and 290 mμ (ϵ 4.56 × 10³)] characteristic of the N-substituted benzotriazole system.[32] This compound is presumed to be 5-methyl-1-benzylbenzotriazole (lit.[33] mp 102–103°).

Anal. Calcd for $C_{14}H_{13}N_3$: C, 75.40; H, 5.88; N, 18.84. Found: 75.27; H, 6.00; N, 18.82.

Nitrosation of N,N-Diethylbenzylamine. N,N-Diethylbenzylamine[34] (24 g, 0.15 mole) was nitrosated by the general procedure. Distillation of the reaction mixture gave 8.34 g of a mixture of benzaldehyde and diethylnitrosamine, bp 80–90° (25 mm), and 13.76 g (57%) of N-nitroso-N-ethylbenzylamine,[7] bp 150–156° (25 mm) with semicarbazide hydrochloride solution and pyridine to give 4 g (16%) of benzaldehyde semicarbazone, mp 222°.

Nitrosation of α-Carboethoxytribenzylamine. α-Carboethoxytribenzylamine (3.49 g, 0.01 mole) was dissolved in 70 ml of glacial acetic acid and stirred at 90° on the steam bath while 20 ml of 7.7 *M* sodium nitrite solution was added over a 0.5-hr period. After stirring with heating for 1 hr, the reaction mixture was poured into 300 ml of water and extracted with three 50-ml portions of ether. The extracts were combined and washed with dilute sodium carbonate solution, water, and saturated salt solution, and were dried over anhydrous sodium sulfate. Analysis of the reaction mixture by vpc showed only benzaldehyde and no ethyl phenylglyoxalate. Attempts to characterize the nitrogen-containing product from this and repeated reactions were unsuccessful, owing to decomposition.

Nitrosation of α-Methyltribenzylamine. α-Methyltribenzylamine[35] (0.01 mole) was nitrosated in the manner described for

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(30) A. D. Cross, F. E. King, and T. J. King, *ibid.*, 2724 (1961).
(31) M. Gomberg and C. C. Buchler, *J. Am. Chem. Soc.*, **42**, 2069 (1920).
(32) R. H. Wiley and K. F. Hussang, *ibid.*, **79**, 4396 (1957).
(33) T. Zincke and A. T. Lawson, *Ann.*, **240**, 130 (1887).
(34) A. Sitka and F. Keil, *Ber.*, **61**, 1690 (1928).

α-carboethoxytribenzylamine. Analysis by vpc showed that the carbonyl portion of the reaction mixture contained benzaldehyde and acetophenone in the ratio 92:8. The nitrosamines would not come off the column.

Nitrosation of Ethyl α-Diethylaminophenylacetate. Ethyl α-diethylaminophenylacetate[36] (23.5 g, 0.1 mole) was nitrosated by the general procedure. Distillation of the extracts from the drowned reaction mixture gave 1.71 g of diethylnitrosamine (which, being very water-soluble, was not completely extracted from the reaction mixture), 2.91 g (16.4%) of ethyl phenylglyoxalate distilling at 56° (0.2 mm) characterized by comparison of an infrared spectrum with the authentic material), and 13.42 g (57%) of ethyl α-(N-ethylnitrosamino)phenylacetate, bp 100–105° (0.3 mm). The last substance gave a positive Liebermann nitroso test and was further characterized by its infrared and nmr spectra, which were entirely consistent with the assigned structure, in which restricted rotation about the N–N bond is present (*e.g.*, two singlets, approximately 0.5 proton each, at τ 3.5 and 4.0, corresponding to the α hydrogen of the phenylacetate moiety, and doubled signals assignable to the N-ethyl group, partly overlapping the multiplets of the O-ethyl group).

Attempted Nitrosation of N,N-Dibenzyl-4-nitroaniline. N,N-Dibenzyl-4-nitroaniline[37] (16 g, 0.05 mole) was heated in 200 ml of glacial acetic acid with stirring on a steam bath while 35 g of sodium nitrite in 50 ml of water was slowly added. After 4 hr of heating, the cooled mixture deposited yellow crystals (15.8 g, 99%), mp 131–132°, undepressed by starting amine.

Attempted Nitrosation of Quinuclidine. A solution of 50 ml of 60% acetic acid solution, 5.8 g of sodium acetate, and 0.9 g of quinuclidine[38] was stirred and heated on a steam bath while 6 ml of 7.7 *M* sodium nitrite solution was slowly added. Stirring and heating were continued for 1 hr, and the mixture was then cooled, carefully basified with 10% sodium hydroxide solution, and extracted with three 50-ml portions of ether. The combined extracts were dried over anhydrous sodium sulfate, and hydrogen chloride was bubbled in. The precipitated hydrochloride weighed 1.1 g, (92%), mp >330°; a portion was basified and converted to the picrate, mp 281–282°, undepressed by quinuclidine picrate.

Attempted Nitrosation of Tribenzylmethylammonium Nitrate. A solution of 13.9 g (3.25×10^{-2} mole) of tribenzylmethylammonium iodide[39] in 50% ethanol was added to a water solution of 5.53 g (3.25×10^{-2} mole) of silver nitrate and the silver iodide removed by filtration. Evaporation of the filtrate gave 9.9 g (84%) of tribenzylmethylammonium nitrate (mp 199–200°), which was heated with 100 ml of acetic acid to about 95° on the steam bath, and 35 ml of 7.7 *M* sodium nitrite solution was then added over a 45-min period. After 2 hr of stirring while heating, the mixture was evaporated to dryness, and the residue was digested with 100 ml of acetone. Evaporation of the acetone solution gave a solid mixture, which was treated with cold water, leaving 7 g of water-insoluble material, mp 195–197° after recrystallization from ethanol, undepressed by a sample of the starting nitrate. No other organic substance (except sodium acetate) could be detected in the other filtrates and solids.

Gases from Nitrosation of Tribenzylamine. The gaseous products from the nitrosation of 1 g (0.64 mmole) of tribenzylamine were swept from the reaction vessel with carbon dioxide into the bottom of a gas-collection tower containing 800 g of potassium permanganate and 200 g of potassium hydroxide in 1200 ml of water. The gas was then transferred to another trap held at liquid nitrogen temperature and distilled from it into the final collection vessel. Mass spectrographic analysis of samples (75 ml, STP) from two identical experiments showed the presence principally of nitrous oxide (mass 44) contaminated with nitric oxide, argon, and nitrogen.

Tribenzylamine Oxide. A solution of tribenzylamine (28 g, 0.1 mole) in 100 ml of glacial acetic acid and 15 ml of 30% hydrogen peroxide was stirred at 60° for 24 hr and then cooled; a pinch of palladium on charcoal was added to decompose the excess peroxide. The solution was filtered and taken to dryness under reduced pressure. Trituration of the resulting white solid with ether gave 27.7 g (94%) of tribenzylamine oxide, mp 138°.

Anal. Calcd for $C_{21}H_{21}NO$: C, 83.15; H, 6.99; N, 4.62. Found: C, 83.04; H, 7.04; N, 4.52.

Nitrosation of Tribenzylamine Oxide. Tribenzylamine oxide (15 g, 0.05 mole) was nitrosated in the same manner described for the tertiary amines in the general procedure. The aqueous reaction mixture was poured into 200 ml of water and extracted with three 75-ml portions of chloroform. The combined extracts were washed with 25% potassium carbonate solution, dried over sodium sulfate, and distilled to give 3 g (48%) of benzaldehyde, bp 65° (13 mm), identified by its infrared spectrum. The residue from the distillation was poured into 50 ml of ethanol and cooled to give 8.23 g (73%) of dibenzylnitrosamine, mp 58°.

In another experiment, tribenzylamine oxide was treated with 1 equiv of nitrous acid, but only starting material and the foregoing nitrosation products could be detected; no tribenzylamine was isolated.

α-d_2-Tribenzylamine. A 1-l. three-necked flask equipped with a pressure-compensated dropping funnel, Trubore stirrer, and a reflux condenser was flamed out twice under evacuation and filled with dry nitrogen. About 300–400 ml of ether was distilled into the flask from lithium aluminum hydride and the flask charged with 2.75 g (0.65 mole) of 98% lithium aluminum deuteride (Metal Hydrides, Inc.). A solution of 30.1 g (0.1 mole) of N,N-dibenzylbenzamide[40] in 80 ml of dry benzene was added dropwise to the stirred mixture over a 75-min period. The stirring mixture was refluxed for 7 hr, cooled, and hydrolyzed with 6 ml of water followed by 4.8 ml of 10% sodium hydroxide. The inorganic salts were removed by filtration and the ether stripped to leave an oil, which solidified upon addition of ethanol. The amine was recrystallized twice from alcohol to give 16.4 g (57%) of α-d_2-tribenzylamine, mp 90–92° (undepressed by an authentic sample).

Nitrosation of α-d_2-Tribenzylamine. α-d_2-Tribenzylamine (14.5 g, 0.05 mole) was nitrosated by the general procedure, except that the temperature was held at 95°. The aqueous mixture from the nitrosation was poured into 300 ml of water and extracted with three 125-ml portions of chloroform. The combined extracts were washed with water, 10% sodium bicarbonate solution, and saturated salt solution. After drying (sodium sulfate), the chloroform was removed under nitrogen, and the residue was distilled to give 3.21 g (58%) of benzaldehyde, bp 64–65° (12 mm). Three samples were prepared for deuterium analysis by diluting 0.2 ml of benzaldehyde to 2 ml, with carbon tetrachloride.

The residue from the distillation was taken up in ethanol and treated with Norit; cooling produced 7.9 g (71%) of dibenzylnitrosamine,[26] mp 58–59°.

Analysis for Deuterium Content. The deuterium content of the starting α-d_2-tribenzylamine was determined by the method of Keston[10a] to be 8.4 mole % (theoretical maximum 9.52%); the percentage of α deuteration is thus $8.4/9.52 \times 100 = 88.5\%$.

The infrared method and data of Wiberg[10b] were used to determine the proportion of deuteriobenzaldehyde in the mixture. The average % transmission at 2070 cm^{-1} for the three samples was 93.93%, which corresponds to 7.8% deuteriobenzaldehyde; at 2100 cm^{-1}, transmission was 92.2%, corresponding to 7.8% deuteriobenzaldehyde.

A confirmation of the percentage of α deuteration in the dibenzylnitrosamine was accomplished by means of nuclear magnetic resonance. Dibenzylnitrosamine shows complex aromatic proton absorption at about τ 2.9, and two singlets at τ 4.88 and 5.45, which arise from the methylene protons. A comparison of the area under the first peak compared with the areas under the peaks for the methylene protons in the deuterated compound gave a rough value of 7% undeuterated dibenzylnitrosamine.

If the starting α-d_2-tribenzylamine were 100% α dideuterated, then the statistical maximum amount of deuteriobenzaldehyde would be 33%. The amine was 88.5% α dideuterated, however, so the statistical maximum deuteriobenzaldehyde content is $(33.33) \times (88.5\%) = 29.5\%$, and $k_H/k_D = 29.5/7.8 = 3.78$.

Nitrosation of Tertiary Amines with Nitrosyl Compounds. Apparatus. All the apparatus used in experiments that fall under this general heading was either baked out in an oven at 140° for 24 hr prior to use or flamed out twice while evacuated.

Solvents. Ether and benzene were dried by refluxing over lithium aluminum hydride and were distilled directly into the reaction vessel. Chloroform was purified by extracting with water eight times, drying over calcium chloride, and distilling from calcium chloride. Dimethyl sulfoxide was distilled from and stored over molecular sieves. Petroleum ether (reagent grade) was not purified but used from a freshly opened bottle.

(35) K. Parck, *J. Prakt. Chem.*, [2] **86**, 287 (1912).
(36) J. Klaso, *Arch. Pharm.*, **285**, 401 (1952).
(37) R. D. Desai, *J. Indian Chem. Soc.*, **5**, 426 (1928).
(38) G. R. Clemo and T. P. Metcalf, *J. Chem. Soc.*, 1989 (1937).
(39) L. Birkofer, *Ber.*, **75**, 436 (1942).
(40) G. Wittig and H. Ludwig, *Ann.*, **989**, 55 (1954).

Reagents. Tribenzylamine[25] was recrystallized from ethanol twice and dried *in vacuo* over phosphorus pentoxide. N-Methylpiperidine was prepared according to Clarke[41] and distilled from sodium prior to use. Nitrosyl chloride was obtained from Olin Matheson Co. and redistilled twice prior to use. Nitrosyl fluoroborate was prepared by the method of Wannagat and Hohlstein[42] and dried over phosphorus pentoxide *in vacuo* prior to use.

Reaction of Tribenzylamine with Nitrosyl Chloride in Benzene. Tribenzylamine (28 g, 0.1 mole) dissolved in 15 ml of benzene was added over a 20-min period to a stirred solution of 25 ml of nitrosyl chloride in 250 ml of benzene held at 6°. After 30 min, the drying tube was removed from the flask, and the mixture was filtered rapidly through a sintered-glass filter. The precipitate was washed with 250 ml of benzene and dried in a vacuum desiccator; weight 20 g. The filtrate was concentrated by distillation of some benzene and nitrosyl chloride. Ether was distilled into the residual solution (50 ml); a second precipitate developed after about 100 ml of ether had distilled. The first precipitate was treated with dilute base and extracted with ether. Concentration of the extracts left an oil which soon solidified; it was recrystallized from alcohol, and then had mp 91°, undepressed by tribenzylamine. The second precipitate was so hygroscopic as to preclude meaningful weighing; when a portion of it was treated with hot water, an oil appeared with dissolution of the solid. The oil was extracted into ether, the ether was removed, and the residue was treated with 2,4-dinitrophenylhydrazine reagent. The resulting orange crystals were recrystallized from xylene, and melted at 233–235°, undepressed by benzaldehyde 2,4-dinitrophenylhydrazone. The water solution from this treatment was concentrated and cooled to yield white crystals, which melted at 255–256°, undepressed by authentic dibenzylamine hydrochloride. No other products could be detected in the other filtrates.

In a second, otherwise similar, experiment, 20 ml of nitrosyl chloride was used in a total volume of 325 ml of benzene, and the benzene filtrate from the original reaction was distilled directly instead of being diluted with ether. There were obtained 2.3 g (22%) of benzaldehyde, bp 70–75° (12 mm), and 4.76 g (21%) of dibenzylnitrosamine, bp 118–122° (0.5 mm), mp 56–57°. The original precipitate was treated with aqueous alkali and then distilled to give 13.7 g (48%) of tribenzylamine, mp 91°, and 3.9 g (20%) of dibenzylamine, bp 88–92° (0.12 mm), hydrochloride mp 255–256°. A third experiment conducted exactly similarly to the second except for the use of only 8 ml of nitrosyl chloride yielded 2.2 g (20%) of benzaldehyde, 1.3 g (5.8%) of dibenzylnitrosamine, 16.55 g (50%)of recovered tribenzylamine, and 2.50 g (13%) of dibenzylamine.

The Reaction of Tribenzylamine with Nitrosyl Fluoroborate in Chloroform. Apparatus. The reaction vessel was an Ace Glass Crystallizer Assembly, consisting of a 100-ml jacketed flask whose bottom contained a fritted glass filter leading to a stopcock. The flask was fitted with a dropping funnel, ground-glass mechanical stirrer, thermometer, and a solvent inlet tube. The reaction flask was cooled by a stream of nitrogen which was passed through a cooling coil immersed in liquid air and into the jacket of the flask.

A. At Room Temperature. A solution of 7.17 g (0.025 mole) of tribenzylamine in 15 ml of chloroform was added dropwise over the course of 45 min to a stirred solution of 2.9 g (0.025 mole) of nitrosyl fluoroborate in 38 ml of chloroform under an atmosphere of nitrogen. Oxides of nitrogen were immediately evolved, and the solution developed a deep red-brown color. After the mixture had stirred for 1.5 hr, 75 ml of petroleum ether was added and a colorless precipitate formed, which was separated by filtration, washed with petroleum ether, and dried *in vacuo* (weight 8.87 g). The filtrates yielded less than 10 mg of material. The precipitate showed infrared bands at 3200 and 1650 cm^{-1} and nmr absorptions ($CDCl_3$) at τ 5.61 (doublet), 4.78, 4.64, 2.62 (two peaks), and 0.57 (singlet). The peak areas of the doublet bore no integra relationship to any of the singlets, but the area under the two singlets at τ 4.64 and 4.78 was four times that under the 0.57 peak.

A 5-g sample of the precipitate was treated with 50 ml of warm water and extracted with ether. Evaporation of the dried ether extract yielded an oil, which was taken up in 30 ml of ethanol and treated with excess 2,4-dinitrophenylhydrazine reagent. A precipitate of 690 mg (18.4%) of benzaldehyde 2,4-dinitrophenylhydrazone, mp 236°, formed (melting point undepressed by an authentic sample). The aqueous extract of the solid was basified and extracted with ether. Evaporation of the dried ether solution left 2.555 g of an oil, which was found by gas–liquid chromatography to be a mixture of 36% of dibenzylamine and 64% of tribenzylamine. Crystallization from ethanol gave 1.307 g (32.3%) of tribenzylamine, mp 90°. The filtrate was evaporated to an oil, taken up in ether, and treated with dry hydrogen chloride to give 0.607 g of crude hydrochloride, which was recrystallized from ethanol to give 268 mg (9.67%) of dibenzylamine hydrochloride, mp 256°.

Another 2-g sample of the reaction product was placed in 20 ml of water with 5 ml of ethanol and 1 g of sodium hydroxide and heated briefly. The mixture was extracted with five 30-ml portions of ether. The dried ether solution was found by glpc to contain a mixture of 22.4% of benzaldehyde, 29.1% of dibenzylamine, and 48.5% of tribenzylamine; evaporation of the ether left 1.43 g of mixture.

B. At −50 to −55°. The reaction flask was charged with 2.9 g (0.025 mole) of nitrosyl fluoroborate and 38 ml of freshly distilled chloroform and flushed with dry nitrogen; a positive pressure of nitrogen was maintained for the duration of the experiment. The stirrer was started and part of the nitrosyl fluoroborate dissolved. The flask was cooled to −50 to −55°, and a solution of 7.17 g (0.025 mole) of tribenzylamine in 15 ml of chloroform was added dropwise over a 0.5-hr period. A reddish precipitate formed and the mixture was stirred at −50° for an additional 1.5 hr. The solid was rapidly filtered from the chloroform solution and quickly washed with 50 ml of chloroform in two portions at −50° (combined filtrates A). The solid was then suspended in 50 ml of cold petroleum ether and allowed to warm to room temperature with stirring. Evolution of oxides of nitrogen was noted during this time. The resulting white solid was filtered, washed with petroleum ether, and dried *in vacuo;* weight 3.98 g (combined filtrates B).

The white solid had nmr and infrared spectra similar to those obtained from the reaction at room temperature. A 2-g sample was hydrolyzed with alcoholic sodium hydroxide as previously described. The oil obtained weighed 805 mg, and was found by glpc to be a mixture of 16.8% of benzaldehyde, 15.4% of dibenzylamine, and 67.8% of tribenzylamine.

Filtrate A was poured into 300 ml of petroleum ether, precipitating 1.175 g of a solid which, upon treatment with base and extraction into ether, yielded 751 mg of an oily mixture of dibenzylamine (3.3%) and tribenzylamine (96.7%) (benzaldehyde, if present, could not be detected in small amounts, owing to the proximity of its glpc peak to the solvent peak). The petroleum ether filtrate gave 4.714 g of unreacted tribenzylamine, mp 89°, upon evaporation.

Filtrate B yielded only a 10-mg residue when evaporated.

Gas–liquid chromatography for the nitrosyl fluoroborate experiments was performed on a MicroTek 2000 R gas chromatograph equipped with a thermal conductivity detector. All analyses were done on a 4-ft column of 10% S.E. 30 on Chromosorb. The column temperature was held at 175° for 4 min after injection of the sample and then raised to 230° at a rate of 50°/min. The flow rate was 100 cc/min, and the inlet and detector temperatures were 300 and 275°, respectively. Under these conditions the retention times of the authentic substances were: benzaldehyde, 0.5 min; dibenzylamine, 4.8 min; and tribenzylamine, 10.0 min.

Formation of α-Cyanotribenzylamine from Tribenzylamine. Tribenzylamine (14.3 g, 0.05 mole) was treated with 5.8 g of nitrosyl fluoroborate at room temperature as described above, except that the solid product was not dried but was dissolved in 150 ml of dimethyl sulfoxide, to which 6 g of potassium cyanide was added, and the mixture was then stirred overnight. The mixture was poured into 600 ml of water and extracted with three 150-ml portions of ether. The combined extracts were washed with water and saturated salt solution. The ether was stripped off after drying over sodium sulfate, and the resulting oil was taken up in ethanol. Upon cooling, a solid, mp 69–81°, separated; it was recrystallized four times from petroleum ether (bp 60–75°) to give 10 g (0.032 mole, 64%) of α-cyanotribenzylamine, mp 102.5–104°, undepressed by an authentic sample.

Hydrolysis of the Red Tribenzylamine–Nitrosyl Fluoroborate Adduct. The red precipitate was prepared as described above, except that it was covered with 150 ml of petroleum ether and the temperature was held at −45° for the remainder of the experiment. A dropping funnel was charged with 25 ml of precooled 16.7% alcoholic potassium hydroxide solution, which was slowly added to the cold, stirred mixture. The mixture was stirred for 30 min after the addition was complete, and was then allowed to come to

(41) H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4576 (1933).
(42) U. Wannagat and G. Hohlstein, *Ber.*, **88**, 1842 (1955).

room temperature with stirring. The mixture was then poured into a separatory funnel containing water and ether and extracted with ether. The aqueous portion was diluted up to 1 l. with distilled water and analyzed for nitrite ion using the method of Kolthoff and Belcher.[43] The average molarity of nitrite ion of the solution from a number of determinations was 0.0140. The organic layer from the extraction was stripped of solvent, giving tribenzylamine (5.2 g, 36%, 0.0181 mole), melting at 90°, undepressed by an authentic sample. The tribenzylamine to nitrite ion ratio was thus 1.3/1. In a duplicate experiment, it was determined (more reliably it is believed) that the aqueous solution was 0.013 *M* in nitrite ion, and the organic layer yielded 3.55 g (0.0128 mole) of tribenzylamine. The tribenzylamine to nitrite ion ratio was 0.985/1.

Lithium Aluminum Hydride Reduction of the Tribenzylamine–Nitrosyl Fluoroborate Adduct. The reddish adduct was prepared at −45° as described, except that it was covered with about 200 ml of dry ether. While the temperature was held at a −45° and the mixture stirred, 60 ml of a saturated solution of lithium aluminum hydride in ether (about 0.75 *M*) was added slowly. The characteristic red color of the adduct slowly disappeared and a white suspension resulted; it was stirred at −45° for 90 min, then warmed to −20° and hydrolyzed carefully with 6 ml of water followed by 4.8 ml of 10% sodium hydroxide solution. The stirring mixture was allowed to warm to room temperature, and the precipitate was filtered off. The ether was removed from the filtrate by distillation, and the residue was taken up in ethanol and cooled to give some tribenzylamine.

The precipitate from the filtration was digested with five successive 50-ml portions of absolute ethanol, evaporation of which left nothing.

In another experiment, the mixture that resulted from the hydride addition was allowed to warm to room temperature prior to hydrolysis, but the results were the same.

Reaction of N-Methylpiperidine with Nitrosyl Fluoroborate in Ether at −45°; Treatment of the Product with Lithium Aluminum Hydride. A flask fitted with a drying tube, stirrer, and dropping funnel containing 9.9 g (0.1 mole) of N-methylpiperidine was charged with 100 ml of ether and cooled to −45°. Nitrosyl fluoroborate (11.8 g, 0.1 mole) was then added, and the mixture was stirred for 15 min prior to the dropwise addition of the N-methylpiperidine. After 90 min, the addition was complete and a yellow orange solid had formed. Stirring was continued for an additional 45 min before the dropwise addition of 70 ml of a saturated solution of lithium aluminum hydride in ether was commenced. The mixture was stirred at −45° for 1 hr and then the temperature was allowed to rise. When the temperature in the flask reached about 0°, a rather exothermic reaction ensued. The mixture was stirred at room temperature for 1 hr and hydrolyzed with 8 ml of water followed by 6 ml of 10% sodium hydride solution.

The salts were removed by filtration and digested in absolute alcohol. Concentration of the alcoholic extracts gave a hygroscopic mass, which was treated with dilute base and extracted with ether. The extract was concentrated and treated with picric acid, yielding a picrate of mp 223–225°, undepressed by N-methylpiperidine picrate. The aqueous mixture from the extraction was brought to pH 7 with dilute fluoroboric acid and then taken to dryness by evaporation in a stream of nitrogen while heating on the steam bath. Digestion of the resulting salts with alcohol extracted nothing.

The ethereal solution from the reaction was dried over sodium sulfate and distilled to give a fraction boiling at about 80–90°, identified as N-methylpiperidine by the melting point of its picrate, 223–225°, undepressed by authentic material. Distillation of the residue at 10 mm pressure gave about 1 g of a liquid boiling at 96–100°. It was unreactive toward gaseous hydrogen chloride, but evolved a flammable gas, presumably hydrogen, when treated with aqueous acid. The liquid, which burned with a green flame, and showed strong infrared absorption in the region 2400–2250 cm^{-1}, was concluded to be the BH_3 adduct of N-methylpiperidine.

Anal. Calcd for $C_6H_{18}NB$: C, 63.90; H, 14.33; N, 12.48. Found: C, 64.14; H, 14.64; N, 12.76.

Another experiment was performed in the same manner except that the mixture was not allowed to warm above −15° after the hydride addition was complete. The mixture was hydrolyzed at this temperature, and then was allowed to warm from −15° to room temperature. The formation of an adduct was not observed, and only N-methylpiperidine could be isolated.

N-Methyl-N,N-pentamethylenehydrazinium fluoroborate was prepared by treating the corresponding iodide[44] with silver fluoroborate in water. The fluoroborate could be reconverted to the iodide by treatment with sodium iodide in alcohol, and melted at 146–150°.

Treatment of N-Methyl-N,N-pentamethylenehydrazinium Fluoroborate with Lithium Aluminum Hydride in Ether. The hydrazinium salt (6.5 g) suspended in 50 ml of ether was cooled to −10°, and the 70 ml of saturated ethereal lithium aluminum hydride solution was slowly added with stirring. After 1 hr the temperature was allowed to rise to 20° and stirring was continued for 1 hr more. The mixture was then refluxed for 30 min, cooled, and hydrolyzed with 6 ml of water followed by 4.8 ml of sodium hydroxide solution. The salts were filtered off and digested in absolute ethanol to give a small amount of the unchanged quaternary hydrazine. The ether solution was distilled to give a small amount of N-methylpiperidine (identified by its picrate) followed by N-methylpiperidine–borane, bp 100° (11 mm), identified by its infrared spectrum.

(43) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, p 141.

(44) L. Knorr, *Ann.*, **221**, 297 (1883).